Bol. Grupo Español Carbón

Síntesis de electrocatalizadores basados en perovskitas, espinelas y materiales carbonosos para reacciones de almacenamiento y producción de energía

Synthesis of electroacatalysts based on perovskites, spinels and carbon materials for energy storage and production

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Objectives and Novelty

Currently, there is a huge interest in developing new technologies eco-friendlier and more sustainable to obtain energy and suppress the dependence on fossil fuels. In this context, electrochemical devices such as fuel cells, metal-air batteries and electrolyzers are presented as promising alternatives to store and produce energy. However, they require electrocatalysts based on noble metals to proceed with the involved reactions, being this one of the main problems in completely implanting these technologies at a large scale. Therefore, it is essential to develop alternative electrocatalysts based on abundant and cheap elements. Among the different alternatives, perovskite and spinel-based materials are considered a great option because it is possible to tailor their physicochemical and electrochemical properties and as consequence their electrocatalytic behaviour.

Despite the great properties of metal oxides, these have two main disadvantages related to their low surface area and electrical conductivity that limit their application by themselves. To mitigate these drawbacks, they require to be mixed with carbon materials which can solve these problems and enhance the electrocatalytic behaviour. However, the role of carbon materials is not only mitigating the described problems, but it might also participate in the reactions. Thus, the main objective of this Doctoral Thesis is to synthesize perovskite- and spinel-based materials active for the electrochemical reactions (oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER)), mixed these metal oxides with carbon materials (mainly carbon black) and to understand the role of carbon materials in the reaction mechanisms.

Results

The doping of perovskite-based materials ($LaBO_3$, where B is a 3d transition metal) with another 3d transition metal is expected to enhance the oxygen molecular reactions. For this purpose, the $LaMn_{1-x}Co_xO_3$ perovskites were synthesized by a sol-gel method and characterized by different techniques. The results indicated that the cobalt substitution affects the crystallographic parameters and surface cation composition. The cobalt substitution stimulates the enrichment of B cations with higher oxidation states, which can affect positively the ORR activity. However, low cobalt content seems to enhance the ORR catalytic activity of the perovskite oxides (Figure 1). For OER, it is preferable to have more Co^{3+} species but to have a bifunctional catalyst the concentration of cobalt must be low (x=0.3 and 0.5). The carbon black (Vulcan) was reported to have an important role in the reactions due to the formation of C-O-B species during the physical mixing, which favour the electron transfer enhancing the catalytic performance. Moreover, the carbon material can act as a co-catalyst in the ORR by producing HO_2^-, whereas in the OER can release the active sites by spill-over of the O_2.

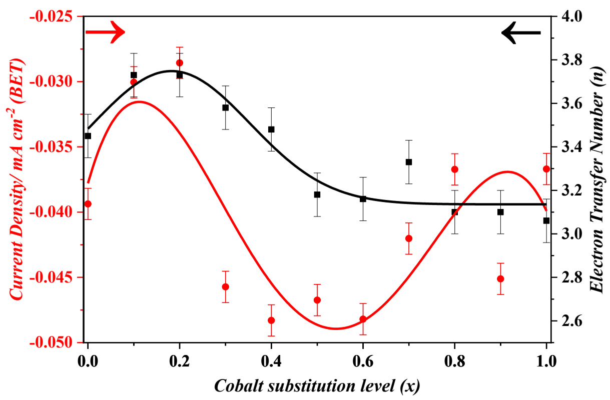

Figure 1. Change in BET-normalized current density and electron transfer number with increasing cobalt content in $LaMn_{1-x}Co_xO_3$ perovskite materials. The data were collected at 0.4 and 0.7 V for current density and electron transfer number, respectively.

The same study was performed for the $LaNiO_3$ perovskite obtaining the $LaNi_{1-x}Co_xO_3$ perovskites. It was observed that on increasing the cobalt content the ORR activity increases due to the higher Co^{3+} content, whereas the OER decreases due to the lower Ni^{3+} concentration. It was also reported that the presence of cobalt increases the oxygen vacancies that favour electron transfer and improve the catalytic activity in ORR. Thus, to obtain a bifunctional electrocatalyst is important to have both cations in the material, also this provides higher stability in both reactions.

Apart from cation doping, there are other approaches to enhance the electrocatalytic activity. One approach is the synthesis of a $LaMnO_3$ perovskite by changing the ratio of La:Mn according to the formula $La_{1-x}MnO_z$. It was observed that the x value determines the formation of the type of spinel (cubic or rhombohedral) and the average crystallite size, as well as the number of Mn active sites. Among the different metal oxides, the sample $La_{0.6}MnO_z$/Vulcan exhibited the best ORR performance and showed good stability. The great activity was related to the low average size of crystallites for the active phases, high concentration of surface manganese, the accurate concentration of Mn^{4+} species and oxygen vacancies.

Another approach to enhance the catalytic activity is through post-synthesis treatments. For this, copper ferrite nanospheres (CFNS) were synthesized by a solvothermal method. Then, they were calcined at different temperatures between 200-600 ºC to generate different surface chemistry and crystal phases. Among the different samples, the sample calcined at 400 ºC exhibits a greater electrochemical performance. This is associated with the presence of a cubic spinel structure and the formation of a copper active phase (tenorite). Moreover, its acceptable BET surface area and the smaller crystallite size of the phases affect positively the electrocatalytic performance.

To study HER, Co_3O_4 and $CuCo_2O_4$ spinel nanoparticles were synthesized by a drop-casting method employing mesoporous silica. The as-prepared nanoparticles were mixed physically with a microporous activated carbon to enhance the electrochemical performance. It was observed that copper favours the chemisorption of water molecules due to the presence of oxygen vacancies and Co^{3+} species. Moreover, the microporous carbon might participate actively in HER by acting as a hydrogen reservoir providing H_{ads} to the oxide nanoparticles, making the hybrid materials promising electrocatalysts for HER.

Conclusions

This Doctoral Thesis has shown the great catalytic performance of perovskite and spinel oxide materials in different electrocatalytic reactions, making them potential alternatives to commercial noble metal-based electrocatalysts. Moreover, several strategies have been carried out in this PhD Thesis to tailor the physicochemical properties of the metal oxides in order to have a higher concentration of active sites on the surface for better catalytic behaviour. Furthermore, it has been proven the active role of carbon materials in electrochemical reactions, which is necessary to enhance the electrocatalytic performance of metal oxides. Therefore, this Doctoral Thesis presents a promising outlook for obtaining potential alternative materials for the proposed reactions, and different strategies to improve the catalytic performance, which can be further used for future research.

Acknowledgments

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Related Publications

[1] J.X. Flores-Lasluisa, J. Quílez-Bermejo, A.C. Ramírez-Pérez, F. Huerta, D. Cazorla-Amorós, E. Morallón. *Copper-doped cobalt spinel electrocatalysts supported on activated carbon for hydrogen evolution reaction.* Materials, 12-8, pp. 1302-1315 (2019)

[2] J.X. Flores-Lasluisa, F. Huerta, D. Cazorla-Amorós, E. Morallón. *Structural and morphological alterations induced by cobalt substitution in $LaMnO_3$ perovskites.* Journal of Colloid and Interface Science, 556, pp. 658-666 (2019)

[3] J.X. Flores-Lasluisa, F. Huerta, D. Cazorla-Amorós, E. Morallón. *Carbon material and cobalt-substitution effects in the electrochemical behavior of $LaMnO_3$ for ORR and OER.* Nanomaterials, 10-12, pp. 2394-2416 (2020)

[4] J.X. Flores-Lasluisa, D. Salinas-Torres, M.V. López-Ramón, M.A. Álvarez, C. Moreno-Castilla, Cazorla-Amorós, E. Morallón. *Copper ferrite nanospheres composites mixed with carbon black to boost the oxygen reduction reaction.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 613 (2021)

[5] J.X. Flores-Lasluisa, F. Huerta, D. Cazorla-Amorós, E. Morallón. *Manganese oxides/$LaMnO_3$ perovskite materials and their application in the oxygen reduction reaction.* Energy, 247-123456 (2022)

[6] J.X. Flores-Lasluisa, F. Huerta, D. Cazorla-Amorós, E. Morallón. *Transition metal oxides with perovskite and spinel structures for electrochemical energy production applications.* Environmental Research, 214-113731 (2022

The full PhD Thesis can be downloaded from: *http://rua.ua.es/dspace/handle/10045/125330*